METHOD OF HIGHLY SENSITIVE ANALYSIS OF
NUCLIDES BY MULTIPLE GAMMA-RAY DETECTION

BACKGROUND OF THE INVENTION

This invention relates to the application of multiple
gamma-ray detection to qualitative and quantitative
determination of radionuclides or nuclides in samples
radioactivated by neutrons or other particle rays or gamma-
rays. The multiple gamma-rays emitted from the nuclides
are measured simultaneously and information is taken for a
pair of gamma-rays from each nuclide, thereby analyzing the
nuclides at higher resolution than the conventional
measurement of gamma-rays.

According to the invention, concurrent gamma-rays
emitted from radionuclides are counted simultaneously with
a multiple gamma-ray detector assembly consisting of a
plurality of gamma-ray detectors to make a two-dimensional
matrix, which is analyzed to ensure that the nuclides of
interest are separated completely and analyzed
simultaneously.

The resolution that can be achieved by the prior art
method of analysis has been about 1,000 and this is
increased by a factor of 1,000 to 1,000,000 in the improved
method of the invention which analyzes a two-dimensional
matrix. This resolution is high enough to enable complete
separation of nuclides in a sample no matter how many they
are. Consider an unreal situation where a maximum of 2,000
- 3,000 nuclides known today are generated simultaneously
in an accelerator or a reactor; since they each generate

- 1 -

about 10 gamma-rays on the average, the maximum total number of gamma-rays that are emitted is on the order of 10,000 but given the resolution of 1,000,000, their amounts can be determined simultaneously by analysis of a two-dimensional matrix according to the invention.

In the conventional analysis of radioactivity, gamma-rays emitted from radionuclides are measured with a single unit of germanium semiconductor detector to obtain a one-dimensional energy spectrum and the nuclides of interest are identified on the basis of energy and half-life information. The resolution by the germanium detector is about 1,000 at 1 MeV. The number of gamma-rays emitted from one radionuclide is on the order of ten at average and there is no problem with a sample containing a limited number of nuclides. However, a sample containing several tens of nuclides emit as many as several hundred gamma-rays and it is impossible to separate them completely. In particular, weak gamma-rays are blocked by strong gamma-rays and cannot be analyzed.

To analyze non-radioactive samples, they are first radioactivated by particles from an accelerator or a reactor and the gamma-rays emitted from the sample are detected (for qualitative analysis) and their intensity is measured (for quantitative analysis). In this neutron radioactivation analysis method, the sample of interest is radioactivated by neutrons from a reactor and the gamma-rays emitted from the sample are measured with a single unit of high-resolution germanium detector to produce a

- 2 -

one-dimensional spectrum which is analyzed for peaks, thereby performing quantitative determination.

The analyses described above have been conducted in many fields by various methods and the radioactivation analysis method has seen particularly wide use. Since the development of the germanium semiconductor detector in the sixties, radioactivation analysis using gamma-rays capable of high-resolution detection has made great advances and it is now possible to quantify trace elements in various samples including environmental samples, bio-samples and samples for use in space and earth science studies.

Fig. 1 shows a conventional method of gamma-ray measurement by radioactivation. A sample 1 radioactivated by thermal neutrons from a reactor emits gamma-rays which are measured with a single unit of germanium detector 2 to construct a one-dimensional spectrum 3 plotting count (intensity) on the vertical axis and the energy of gamma-rays on the horizontal axis. If the sample contains many elements, this method yields such a complex spectrum that it is often difficult to measure the elements of interest in separate form.

A major problem of the prior art methods is their high susceptibility to interference by concomitant nuclides. If you are lucky enough, there is no overlap between gamma-rays but if the sample contains many nuclides, the spectrum has such a high background that it is very difficult to detect weak gamma-rays.

To eliminate the adverse effects of interfering

nuclides, samples such as spent nuclear fuels that contain many nuclides are usually subjected to chemical separation or differentiation of nuclides by half-life. However, chemical separation usually requires special skills and prolonged time; in addition, it is necessary to determine the yield of chemical separation but this can be a source of errors. Differentiation by half-life is not an ideal method, either. Considerable time is taken to determine the quantity of a nuclide of long half-life and it is quite cumbersome to maintain the detector system throughout that period.

Thus, the conventional techniques are highly susceptible to the interference by concomitant nuclides and samples such as environmental samples that contain many elements have to be subjected to chemical separation in order to eliminate the adverse effects of the interfering nuclides. For chemical separation, its yield must be determined and this in turn necessitates re-radioactivation; hence, chemical separation requires special skills and prolonged time but this can be a source of errors.

In the conventional method of radioactivation analysis, a sample radioactivated by neutrons from a reactor is measured with a single unit of germanium detector to construct a one-dimensional spectrum and the peaks in the spectrum are analyzed to determine the quantities of elements in the sample. If the sample contains many elements, the relative intensity of generated

- 4 -

radioactivity is not distributed among all nuclides present
but assigned to only limited nuclides and it is difficult
to identify trace elements without chemical separation;
however, errors in the percent efficiency of recovery
5   achieved after separation not only affect the result to be
finally obtained, separation also requires sophisticated
skills of chemical analysis.

In the method of neutron radioactivation analysis,
the relative intensity of generated radioactivity is not
10   generally distributed among all nuclides present but
assigned to only limited nuclides and it is often difficult
to perform simultaneous analysis of many trace elements.
For example, bio-samples have strong radioactivity from
^{24}Na, ^{56}Mn, ^{42}K and ^{82}Br and geological samples from ^{24}Na, ^{56}Mn,
15   ^{42}K, ^{46}Sc and ^{59}Fe; hence, in the method of analyzing a one-
dimensional spectrum with a single detector unit, the peaks
of short-lived nuclides are masked by these strong nuclides
and cannot be detected. To deal with this problem,
radioactivity measurement has to be performed after strong
20   radioactive nuclides are removed by chemical separation.
This not only requires sophisticated skills of chemical
analysis; after chemical separation, re-radioactivation has
to be performed in the reactor to determine the percent
recovery of the desired nuclide. A further concern is the
25   possibility that the precision of analysis may be affected
by the process of chemical separation.

SUMMARY OF THE INVENTION

Noting that many radioactive nuclides emit a

- 5 -

plurality of gamma-rays, the present inventors devised a
method of qualitative and quantitative determination of
these nuclides by analyzing a two-dimensional matrix
obtained by measuring them with a multiple gamma-ray
5   detector assembly consisting of a plurality of gamma-ray
detectors. The method achieved 1,000 times as high an
energy resolution as the conventional method of analyzing a
one-dimensional spectrum.

      The two-dimensional matrix method of the invention
10   comprises the steps of detecting a plurality of concurrent
gamma-rays from radioactive nuclides in a sample with two
or more detectors in a multiple gamma-ray detector
assembly, cumulatively adding the energies of a pair of
detected gamma-rays on a two-dimensional matrix, and
15   detecting the peaks. The background of a one-dimensional
spectrum is localized in a two-dimensional plane, being
limited to less than 10 counts in almost all regions;
hence, even very weak peaks are sufficiently detected to
achieve higher detection sensitivity.

20   In addition, the method of the invention does not
require chemical separation or any other artificial
operations and, hence, can be performed on-line with a
computer. Once preliminary calibration has been done for
the energy of each detector and the efficiency of
25   detection, a two-dimensional matrix is generated as the
sample is measured; the position of a particular peak on
the matrix tells the nuclide it represents and, at the same
time, with reference to the nuclear data for each nuclide

- 6 -

that is stored in the computer, the quantity of the
particular nuclide is determined from the intensity of the
peak and real-time display of the result is possible.
Needless to say, the quantities of nuclides having long
5 half-life can be determined at high speed.

Similarly, the present invention enables qualitative
and quantitative analyses of the nuclides in samples that
have been radioactivated with neutrons from an accelerator
or a reactor.

10 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a conventional method of gamma-ray
detection as applied to a radioactivated sample;

Fig. 2 shows the invention method of gamma-ray
detection as applied to a radioactivated sample; and

15 Fig. 3 shows a two-dimensional matrix constructed by
the invention method of gamma-ray detection.

DETAILED DESCRIPTION OF THE INVENTION

(1) Qualitative and quantitative analyses of nuclides in a
sample radioactivated with neutrons

20 Using a multiple gamma-ray detector assembly
consisting of a plurality of germanium semiconductor
detectors, a plurality of gamma-rays emitted from a
radioactivated sample are measured and combinations of two
simultaneously observed gamma-rays are recorded in a
25 computer and then analyzed to construct a two-dimensional
matrix. Combining a gamma-ray having a given energy with a
concurrently observed gamma-ray, one can construct a neat
spectrum which is substantially free from the interference

- 7 -

by gamma-rays from dissimilar nuclides. As a result, there
is no need to perform artificial operations such as
chemical separation and still gamma-rays from trace
elements can be measured without interference by gamma-rays
5 from concomitant nuclides.

Fig. 2 shows the invention method of gamma-ray
detection as applied to a sample 1 radioactivated with
thermal neutrons from a reactor. Gamma-rays simultaneously
emitted from the sample are measured by simultaneous
10 counting with a multiple gamma-ray detector assembly 4 to
construct a two-dimensional matrix 5 which plots the count
(intensity) on the vertical axis, the energy of one gamma-
ray on the horizontal axis, and the energy of the other
gamma-ray on an axis in between the two axes. According to
15 this method, two gamma-rays γ_1 and γ_2 emitted simultaneously
from a radioactive nuclide in the sample are measured
simultaneously with the multiple gamma-ray detector
assembly to construct the two-dimensional matrix rather
than a one-dimensional spectrum. As a result, even a
20 sample containing many nuclides can be analyzed for gamma-
rays at a resolution of 1,000 without chemical separation
or any other artificial operations and this achieves
measurement of nuclides in completely separate form. The
nuclide of interest can be identified by the position
25 determined by the coordinates (γ_1, γ_2) on Fig. 2 and the
amount of its abundance is detected by the height (count)
of the peak in that position.

As Fig. 3 shows, radioactivated ^{152}Eu generates two

- 8 -

gamma-rays simultaneously, one having an energy of 841.6
keV and the other at 121.8 keV. These two gamma-rays were
subjected to simultaneous counting with the multiple gamma-
ray detector assembly to construct a two-dimensional
5   matrix.

     Fig. 3 also shows a graph plotting the energies of
the two gamma-rays on the horizontal and vertical axes.
The inset for the range of 100 - 140 keV on the vertical
axis and the range of 820 - 860 keV on the horizontal axis
10   is shown enlarged below the graph. As is clear from the
enlarged inset, the two gamma-rays from ^{152}Eu having
respective energies of 121.8 keV and 841.6 keV were
recorded simultaneously and the identity of the nuclide
that emitted those gamma-rays could be known by their
15   positions. In this way, the quantities of as many as 49
elements could be determined simultaneously in resolutions
up to the ppb (10^{-9}) order.

     The multiple gamma-ray detector assembly used in the
present invention has such a high detection efficiency that
20   samples taken in quantities on the milligram order suffice
for measurement purposes. Since the method of analysis of
the invention is nondestructive, radioactivated samples can
be subjected as such to measurement and this provides not
only great convenience but also applicability to a wide
25   range of samples. For example, the method has potential
applications in the quantitative determination of trace
metal elements in environmental and bio-samples, as well as
in earth science and space science for analysis of

- 9 -

meteorites.

Dating techniques using ^{129}I (half life of 1.57 x 10^7 yr) and ^{244}Pu (8.08 x 10^7 yr) have recently been proposed and the method of this invention can be applied to analyze these nuclides. Knowledge is increasing about the relationship between the concentrations of trace elements in living organisms and their biological functions. Since the method of the invention is capable of measuring a wide range of elements simultaneously, it can be used to determine the quantities of heretofore unidentifiable trace elements so that their effects are studied for the first time.

(2) Qualitative and quantitative analyses of nuclides in a radioactive sample

Using a multiple gamma-ray detector assembly consisting of a plurality of gamma-ray detectors, a plurality of gamma-rays emitted simultaneously from a radioactive sample were measured and energy information about a pair of emitted gamma-rays was recorded in a computer for each event and then analyzed to construct a two-dimensional matrix. Intensity measurement was done on the matrix. Alternatively, a narrow gate may be set on one of the two axes, one-dimensional spectra are sliced and the intensities of two-dimensional peaks are effectively measured. By preliminary calibration of the energies of gamma-rays and their intensities, the channels and areas of the two-dimensional peaks can be transformed to energy and intensity, respectively. Based on these data, one can

- 10 -

perform quantitative determination of nuclides.

The procedure described can be performed on-line if the detectors are preliminarily calibrated against a standard radiation source. Specifically, a standard radiation source with known energy and intensity is measured and calibration data for energy and detection efficiency are prepared for each detector. As an actual sample is measured, each detector is calibrated for energy so as to construct a two-dimensional matrix. At the same time, the nuclear data for each nuclide that are stored in the computer are referenced to determine the quantities of nuclides from the intensities of peaks in the matrix on the basis of the calibrated data for detection efficiency, whereby the result is displayed on a real-time basis. Needless to say, the quantities of long-lived nuclides can be determined without waiting for the disappearance of short-lived nuclides and this permits faster analysis.

The multiple gamma-ray detector assembly to be used in the invention consists of at least two gamma-ray detectors. Signals from the two detectors are fed to a fast simultaneous counter which chooses only simultaneous counting events. At the same time, the energy information from the two detectors is taken into the computer. On the basis of this information, the correlation between two gamma-rays is represented on a two-dimensional matrix by means of a frequency distribution of events. The two-dimensional matrix may be replaced by any suitable equivalents. The performance of the multiple gamma-ray

- 11 -

detector assembly improves with the increasing number of
detector units and the increasing detection efficiency of
each detector unit. If necessary, the multiple gamma-ray
detector assembly may be combined with a BGO suppressor to
5   suppress the background and provide higher sensitivity.

The following examples are provided for the purpose
of further illustrating the present invention.

Example 1: Quantitative Determination of Trace Elements by
Neutron Radioactivation Method

10   Standard rock samples were irradiated with neutrons
in a reactor and the gamma-rays from the radioactivated
samples were measured with a multiple gamma-ray detector
assembly. The gamma-rays emitted from about 100 mg of each
sample that had been radioactivated for 10 minutes in the
15   reactor were measured with the multiple gamma-ray detector
assembly for about 4 days. Specifically, standard rock
samples JB-1 and JP-1 published by the Geological Survey of
Japan, Agency of Industrial Science and Technology, MITI
(now the National Institute of Advanced Industrial Science
20   and Technology), were irradiated with neutrons in JAERI
Research Reactor JRR-4 and subjected to a four-day
measurement with a multiple gamma-ray detector assembly
"GEMINI" in the tandem accelerator facilities at JAERI
Tokai Research Establishment.

25   The measurement started immediately after the neutron
irradiation and the quantities of as many as 27 nuclides
could be determined simultaneously within a short time; no
artificial operations such as chemical separation were

- 12 -

performed and there was no need to wait for the decay of
short-lived nuclides. The contents of the measured
elements as calculated from the intensities of gamma-rays
agreed with the documented values within the range of
5 errors. The same technique could perform simultaneous
quantification of 49 elements. Since the two-dimensional
matrix had such a reduced amount of background that it
allowed for detection of very weak peaks and the relative
abundances of nuclides that could be determined
10 quantitatively were on the order of 10^{-9} (one billionth).

The multiple gamma-ray detector assembly "GEMINI"
used in Example 1 was a spherical array of anti-Compton
gamma-array detectors each being the combination of a BGO
Compton suppressor and a germanium detector and capable of
15 lower background and higher resolution. GEMINI was
completed in July 1998 and its primary objective is to
measure gamma-rays from highly excited atomic nuclei
produced by various nuclear reactions and to investigate
their internal structures. GEMINI has achieved many
20 results in nuclear spectroscopic experiments using heavy
ion beams at JAERI Tokai tandem accelerator facilities.

The forty-nine elements that could for the first time
be quantitated simultaneously by the new detection method
of the invention were the following: Ag, As, Ba, Br, Ca,
25 Cd, Ce, Cl, Co, Cs, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, I, In,
Ir, K, La, Lu, Mn, Mo, Na, Nd, Ne, Ni, Os, Pt, Ra, Rb, Re,
Ru, Sb, Sc, Se, Sm, Sn, Ta, Tb, Th, Ti, U, W, Yb and Zn;
the detection limits of these elements were 10^{-2} to 10^{-3} on a

- 13 -

weight basis.

On the other hand, the conventional radioactivation method of analysis (using a one-dimensional spectrum) was capable of simultaneous quantification of the following twenty-three elements: Al, Ar, Au, Cr, Cu, Dy, F, Ho, Kr, Mg, Nb, Pd, Pr, Rh, S, Sr, Te, Tl, Tm, V, Xe, Y and Zr; the detection limits of these elements were 10^{-2} to 10^{-3} on a weight basis.

Example 2: Analysis of Actinides

Obtaining basic data for the nuclear transformation of minor actinides constitute an important basic portion of nuclear research. The quantification of minor actinides which is necessary for this purpose has primarily relied upon the measurement of alpha-rays. Alpha-rays need be detected in high resolution since nuclides of similar atomic numbers emit alpha-rays of similar energies. However, alpha-rays lose so large amounts of energy as they pass through a medium that it has been necessary for the sample to be first subjected to chemical separation to remove impurities, then dried out and processed into a thin radiation source. This has not only required special skills, it has sometimes been difficult to achieve high enough separation efficiency.

These problems are free from the multiple gamma-ray detection method and high-precision analysis can be accomplished without chemical separation although the method requires the emission of multiple gamma-rays. As a matter of fact, in the measurement of ^{237}Np standard

radiation source using GEMINI, nuclides of intensities as low as 0.01 Bq could be measured in complete isolation from other nuclides.

Geological samples irradiated with neutrons usually emit strong gamma-rays from ^{24}Na and ^{56}Mn, making it difficult to measure gamma-rays from trace elements. The multiple gamma-ray analysis method of the invention could perform simultaneous measurement of gamma-rays from 27 elements without chemical separation. The contents of the measured elements as calculated from the intensities of gamma-rays agreed with the documented values of the standard rock samples within the range of errors.

These results show that the invention is applicable not only to qualitative analysis but also to quantitative analysis. Among the elements detected, Eu was present in a very small amount of 4 ppb but it could still be measured together with other elements without chemical separation. Given more favorable conditions, the method is applicable to the detection of 49 elements.

A multitude of radionuclides contained in a sample cannot usually be determined quantitatively in a completely separated state for the purpose of quantitative determination. The multiple gamma-ray detection method used in the invention achieves much higher resolution than the conventional method and the nuclides in the sample, no matter how many they are, can be separated and quantified completely without employing chemical separation or other ancillary means.

- 15 -